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In the early phases of this study, investigations were made of the photochemisty of nitrogen heteroaromatic compounds, particularly molecules related to pyridine, quiniline, and acridine. Work with these compounds involved a variety of different types of studies but basically the main thrust was in identifying the photochemically reactive excited states and determining the relative importance of these states. The studies were extended to the quaternary salts of these complexes in which the presence of one or more positive charges gives rise to new reactivity not observed with the free bases.

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Final Report

Grant # DAAG2976G0079

PHOTOCHEMISTRY OF NITROGEN HETEROCYCLES AND THEIR METAL COMPLEXES

Our work in this area can be sub-divided into three different areas. In the early phases of this study we have investigated the photochemistry of nitrogen heteroaromatic compounds, particularly molecules related to pyridine, quiniline, and acridine. Our work with these compounds has involved a variety of different types of studies but basically we have been most intensely involved in identifying the photochemically reactive excited states and determining the relative importance of these states. Our investigations have been extended to the quaternary salts of these complexes in which the excited state levels are rather substantially altered and in which the presence of one or more positive charges gives rise to new reactivity not observed with the free bases. Finally, we have examined the photochemistry of a number of metal complexes of nitrogen heteroaromatics and have been able to identify both the reactive excited states and their characteristic patterns of reactivity in several cases. For clarity, it is best to sub-divide the studies under this grant into these three areas.

Photochemistry of Nitrogen Heteroaromatic Free Bases

Most of the work in this area was actually completed during a previous grant. Nonetheless, it is worth highlighting our findings at this point in view of the overall results obtained. We found for a number of molecules containing the pyridine ring (pyridine, acridine, and various azastilbenes) that the singlet manifold contains two close lying excited states; one

of these is a $^{1}\pi,\pi^*$ state which is quite similar to the lowest excited singlet of the corresponding aromatic molecule both in terms of its spectral characteristics, natural lifetime and energy. In many cases the reactivity of this state is also similar to that observed in the corresponding hydrocarbon. Nonetheless, these excited states are often very short lived and both low luminescence and low total reaction yield from these states are characteristic. The reason for this is a close lying $^{1}n,\pi^*$ state is often populated in competition with reaction from the hydrocarbon state mentioned above. This state is often "spectroscopically hidden" in that its extinction coefficient for the transition is very low and fluorescence from this state is weak or totally missing in most cases. Nonetheless this state may often be the major state in photochemical reactions occurring on direct irradiation of N-heteroaromatics. Reactions observed from these states are typically free radical processes which are initiated by hydrogen abstraction on nitrogen; typical reaction products obtained are products of photoreduction either of the benzene ring or, in the case of azastilbenes, the ethylenic double bond as well as reductive photoaddition products. We have rather extensively reviewed these reactions in a recent volume.[1] Triplet states of N-heteroaromatics appear to be much more like those of the corresponding hydrocarbons in most cases and in most of the compounds we have investigated, there is no evidence for prominent $^{3}n,\pi^*$ state reactivity.

Quaternary Salts of Nitrogen Heteroaromatics.

Attachment of a proton or an alkyl group to nitrogen removes the possibility of low-lying n,π^* states; however, the resulting molecule differs strikingly from the corresponding hydrocarbon in that the resulting positive charge renders the molecule very polar and electron deficient, thus opening the way for new reactions such as attack by nucleophiles and electron transfer processes. In addition, various types of complex formation which frequently occurs with aromatic hydrocarbons have been observed to be a prominent process for these molecules. The process of nucleophilic addition was one of the earliest investigated reactions and it was found that this reaction occurred primarily from excited singlets.[2] Attempts to sensitize triplets of a number of quaternary salts were frustrated by the fact that even where a triplet energy transfer should be exothermic, competing electron transfer from excited sensitizer to triplet to quaternary salt became an important process.[3] It became of interest to determine whether competition between electron transfer and energy transfer was a general process and whether in the case of competition one process would always dominate. In our studies with quaternary salts of N-heteroaromatics as energy or electron acceptors from excited states of potential energy or electron donors we have found that for some molecules both processes exist and in these cases both reactions occur at more or less the "normal" or predicted rates.[3] This study has been an especially useful one in that it has shown that energy transfer, which was formerly thought to be a dominant process where the reaction was energetically favorable can sometimes be circumvented; especially when one is dealing with highly polar molecules.[3] For the N-heteroaromatic quaternary salts it was possible to demonstrate that use of electron-deficient sensitizers could bypass the electron transfer quenching and allow energy transfer once more to become a dominant process.[3]

Complex formation between excited quaternary salts of N-heteroaromatics and various organohalogen compounds was found to be an important process which allowed a heavy atom-induced singlet-triplet intersystem crossing to take place for several molecules.[4,5] For aromatic halogen compounds, it was found that in many cases electron transfer quenching of the excited N-heteroaromatic quaternary salt singlet state would result in formation of a charge transfer excited state which lies intermediate between the localized N-heteroaromatic singlet and triplet excited states.[4,5] The population of this state by quenching with an aromatic containing a bromine, iodine or chlorine atom often resulted in efficient and accelerated population of the isolated triplet state on the N-heteroaromatic quaternary molecule.[4,5] Thus the net effect of electron transfer quenching in cases where the "heavy" halogen atom is substituted on the quencher is enhanced population of N-heteroaromatic compound triplets and reactions thereof. The net quenching process for aromatic halogen compounds is well explained in terms of electron transfer complex formation since rates of the quenching can be easily correlated with oxidation and reduction potentials.[5] Evidently, for the cases where a heavy atom is not available in the aromatic quencher, the complex simply decays to the ground state bypassing the lowest triplet state of the nitrogen compound.[5] Also in cases where the charge transfer state lies lower than the isolated nitrogen compound triplet, the triplet state is not populated - despite the presence of the heavy atom - and only accelerated production of the ground state is observed. Evidently, in all cases production of the electron transfer complex is an irreversible one since the presence of the heavy atom does not influence the quenching process rate; the net effect is only to change the product distribution.

Somewhat similar effects are observed when haloalkanes are used as quenchers for excited singlets of the nitrogen heteroaromatic quaternary salts;[6] in these cases it is clear that interaction of the haloalkane with the excited nitrogen compound cannot produce a charge transfer excited complex. Nonetheless, rapid and efficient quenching does occur and it appears that in these cases an interaction of the ion-dipole type must be occurring.[6]

Interactions such as this have been observed with other polar molecules and appear to be possibly a very general sort of phenomenon. In this case evidently the ion-dipole complex formation evidently brings a halogen close enough to the aromatic to induce a singlet-triplet intersystem crossing so that the net result once again is production of the localized triplet on the nitrogen heteroaromatic. This phenomenon has been observed for both bromoalkanes and iodoalkanes and we suspect that it should be a fairly general phenomenon with other polar molecules.[6] The external heavy atom effect produced in these cases is interesting in that a molecule not involved in the overall photochemistry (the organic halogen compound) strongly controls the excited states populated and their reactivity.

Photochemistry of Metal Complexes in Nitrogen Heteroaromatics.

Our early work in this area was designed primarily in determining what kinds of excited states could be available and react for these complexes.[7,8] Here in addition to the usual π,π^* states available in the aromatic molecule there exists high energy filled levels on the metal and relatively low lying vacant metal orbitals. Thus in addition to the π,π^* states, there are d,d^* and d,π^* states arising through metal localized and metal-ligand transitions respectively. In addition, in certain cases there are possible ligand-metal transitions. In most of our work we have examined complexes where the prominent long wavelength transitions include ligand π,π^* and metal-ligand d,π^* transitions. Since metal d-d transitions are usually weak, the complexes investigated may also have states resulting from these transitions as low energy excited states. With some metal complexes we were able to show that large wavelength affects on the photochemistry could be interpreted as arising from population of different excited states depending upon the exciting wavelength.[7,8] In most of the cases examined, it was found that the wavelength affects were due to rapid reaction of the different excited states rather than to slow excited state interconversion processes.[7,8]

The prominence of long wavelength metal → ligand charge transfer bands encouraged us to investigate the possibility that excited states of metal complexes might be especially good electron donors.[9-12] This proved to be a rather fruitful avenue of investigation since we were able to show that indeed electron transfer quenching is a very prominent reaction for a wide variety of metal complex excited states.[9-12] We were able to show that electron transfer quenching could be made a dominant route of excited state reactivity in many cases and that in fact this could be a very efficient process for the conversion of light energy into potentially stable chemical products. Unfortunately, a potential problem in the utilization of such processes is the rapid back electron transfer reaction which generates ground states of the starting material. Nonetheless, we feel that this is a very promising type of reaction for energy conversion and are actively working on this in research currently underway. Electron transfer quenching was first observed with excited states showing prominent luminescence, particularly $Ru(bipy)_3^{2+*}$.[9-11] Subsequently it was found that a variety of metal complex excited states having different orbital origin and dramatically different emission properties could be quenched by electron donation to a variety of electron acceptors.[12] Both our work and the work of others has demonstrated that excited states of metal complexes can also serve as electron acceptors from a variety of potential electron donors. The work in this area has kindled a wide interest in these reactions. Much of this is presently a very active area of investigation in our laboratories and of several other workers. These reactions have been studied by a variety of techniques, including luminescence quenching, flash spectroscopy, and permanent product observation.

References

1. D. G. Whitten in "Photochemistry of Heterocyclic Compounds," Ed. O. Buchardt, John Wiley and Sons, New York, N.Y., 1976, p. 524.

2. J. W. Happ, M. T. McCall and D. G. Whitten, J. Am. Chem. Soc., 93, 5496, (1971).

3. A. Gutierrez, T. J. Meyer and D. G. Whitten, Mol. Photochem., 7, 349 (1976).

4. A. R. Gutierrez and D. G. Whitten, J. Am. Chem. Soc., 96, 7128 (1974).

5. A. R. Gutierrez and D. G. Whitten, J. Am. Chem. Soc., 98, 6233 (1976).

6. A. R. Gutierrez and D. G. Whitten, J. Phys. Chem., submitted.

7. P. P. Zarnegar and D. G. Whitten, J. Am. Chem. Soc., 93, 3776 (1971).

8. P. P. Zarnegar, C. R. Bock and D. G. Whitten, J. Am. Chem. Soc., 95, 4367 (1973).

9. C. R. Bock, T. J. Meyer and D. G. Whitten, J. Am. Chem. Soc., 96, 4710 (1974).

10. C. R. Bock, T. J. Meyer and D. G. Whitten, J. Am. Chem. Soc., 97, 2909 (1975).

11. R. C. Young, T. J. Meyer, and D. G. Whitten, J. Am. Chem. Soc., 97, 4781 (1975).

12. R. C. Young, T. J. Meyer and D. G. Whitten, J. Am. Chem. Soc., 98, 286 (1976).